Enhancement of total oxidation of isobutene on bismuth-promoted tin oxide catalysts

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The influence of the incorporation mode of Bi_2O_3 to SnO_2 on the total oxidation of isobutene has been investigated. The catalysts have been characterized by XRD and XPS. Although the pure oxides do not exhibit any individual catalytic activity, certain bimetallic systems display substantial catalytic properties. The observed promoting effect of bismuth depends on the nature of the precursor but not on the incorporation medium. Bismuth oxide obtained from bismuth citrate, bismuth nitrate and the complexes with ethylenediaminetetraacetic acid or nitrilotriacetic acid enhances catalytic activity, whereas pure Bi_2O_3 and bismuth acetate do not increase catalytic properties. The formation of the ternary phase, $Bi_2Sn_2O_7$, during the degradation step or during the catalytic test, cannot be excluded although it has never been detected when the calcination temperature did not exceed 803 K. This pure phase displays a very low activity but the catalysts containing at the same time $Bi_2Sn_2O_7$ and SnO_2 show appreciable catalytic performances. The possible intrinsic catalytic influence of highly dispersed Bi_2O_3 in these catalysts is discussed. In addition, several hypotheses are put forward to explain the synergy between SnO_2 and Bi_2O_3: (i) a remote control mechanism based on the cooperation between separate Bi_2O_3 and SnO_2 phases; (ii) the generation, during the reaction, of a highly dispersed ternary $Bi_2Sn_2O_7$phase which cannot be detected, and could either display important catalytic activity itself, or act synergetically with SnO_2.

Keywords: oxidation, tin dioxide, bismuth oxide, remote control

1. Introduction

Cooperative effects between separate oxide phases have been reported on many occasions in the field of partial oxidation of hydrocarbons [1]. They usually result either in increased yields of selective products or in inhibition of deactivation, and have been rationalized mainly through four different mechanisms: (i) formation of a new (mixed) phase at the interface of the two initial phases in contact, (ii) epitaxial matching between selected crystal planes of the two oxides, (iii) surface contamination of one phase by metallic elements from the other phase and (iv) a remote control mechanism based on the activation of molecular oxygen by a donor phase into mobile species (spill-over oxygen) which migrate to an acceptor phase where they create and/or regenerate selective catalytic sites. In the latter case, cooperation is achieved between two separate and non-contaminated phases.

The present work deals with the observation of cooperative effects in the system Bi_2O_3–SnO_2; bismuth(III) oxide is known as a typical donor of spill-over oxygen [2], and tin(IV) oxide, which has previously been reported to act as donor or acceptor phase according to ref. [3], plays here the role of the acceptor oxide. Cooperation between these two oxides is therefore assumed to occur.

Tin dioxide has been mentioned as catalyst in several partial oxidation reactions. For example, the SnO_2–MoO_3 system is performant in dehydration and dehydrogenation of 2-butanol [4,5] and isopropanol [6] and in the selective oxidation of propene [6]. The association SnO_2–Sb_2O_4 is efficient for the selective oxidation of isobutene into methacrolein [8–10]. The only interesting role of pure bismuth oxide as catalyst is its activity in the dimerization of propene into hexadiene [11]. The choice of the binary system Bi_2O_3–SnO_2 is furthermore related to the fact that Bi_2O_3-promoted SnO_2 systems were recently proposed as new chemical sensors for the online detection of CO, CO_2 and formaldehyde in air [12–14].

The two major objectives of this paper are (i) to present experimental data suggesting that the concept of cooperation between separate oxide phases also applies to the field of total oxidation, and (ii) to show that the choice of appropriate Bi-containing precursors allows one to modulate the observed synergetic effects. Because the investigated effects could be assigned also to the formation of the ternary oxide phase bismuth pyrostannate, $Bi_2Sn_2O_7$, additional experiments were carried out on the influence of this phase on the catalytic properties.

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2. Experimental

2.1. Preparation of SnO_2

Tin(IV) dioxide was prepared according to a literature procedure [15,16], from HCl solutions of tin(IV) chloride (Janssen, 98%) in the presence of urea. The starting solution was filtered through 0.22 μm Millipore membranes to remove possible contaminants. Aging was carried out in polyethylene flasks at 353 K for 6 days. After this treatment, the obtained dispersion was cooled to room temperature and submitted to ultrafiltration. The collected precipitate was washed repeatedly with distilled water. The obtained powder was finally dried at 353 K and further calcined at 803 K for 20 h under controlled air flow (1 ℓ/min). SnO_2 samples prepared by this way present specific surface areas in the range 10–15 m^2/g after calcination. Their powder X-ray diffraction patterns are consistent with the cassiterite phase.

2.2. Bismuth-containing precursors

Several Bi(III) compounds were selected as precursors for the formation of Bi_2O_3 [17]: Bi(III) citrate (commercial, UCB 99%, noted Bi(Hcit)), Bi(III) nitrate pentahydrate (commercial, Fluka 99%, noted $Bi(NO_3)_3$), Bi(III) triacetate (noted $Bi(OAc)_3$) and the chelate-type complexes with ethylenediaminetetraacetic acid (noted Bi(Hedta)) and nitrilotriacetic acid (noted Bi(nta)).

A published literature procedure [18] was used for the synthesis of $Bi(OAc)_3$. The Bi(Hedta) complex was obtained by dissolving commercial Bi_2O_3 in nitric acid, and adding an aqueous solution containing the stoichiometric amount of ethylenediaminetetraacetic acid (H_4edta, Merck 99.4%). The final pH was about 0.5. The formation of the Bi(Hedta) complex was checked independently in the presence of xylenol orange. The Bi(nta) complex was obtained according to the same procedure by using nitrilotriacetic acid (H_3nta, Fluka 99.5%).

2.3. Preparation of the catalysts

Bi_2O_3-promoted SnO_2 catalysts were prepared from the various Bi-containing precursors, introduced in amounts corresponding to a final loading of 10 wt% Bi_2O_3 on the SnO_2 support. Depending on the precursor used, two different procedures were applied to prepare these biphasic catalysts.

Catalysts prepared from Bi(III) acetate were obtained according to a deposition procedure in which particles of this precursor were put in contact with SnO_2 in dry *n*-heptane. These experiments were carried out under an atmosphere of dry nitrogen to prevent the hydrolysis of the bismuth(III) carboxylate. In this procedure, the appropriate amount of bismuth(III) triacetate was first dispersed at room temperature in 100 ml heptane under ultrasonic stirring for 15 min. Tin(IV) dioxide was then added to the former slurry and the mixture was submitted to a further sonication for another 15 min period. The hydrocarbon was subsequently removed very slowly under vacuum and continuous stirring at room temperature. The catalyst prepared from Bi citrate was obtained similarly by dispersion in *n*-heptane but without operating in nitrogen.

In the preparations based on the use of bismuth nitrate, edta and nta complexes, the appropriate amount of tin dioxide was first dispersed at room temperature under ultrasonic stirring in the aqueous solution containing the corresponding Bi-precursor. Water was then removed slowly under continuous stirring upon reduced pressure heating at 353 K.

To look at the influence of the incorporation medium on the catalyst properties, a further catalyst was prepared by dispersing tin dioxide in an aqueous slurry of bismuth citrate (noted Bi(Hcit)*); the same effect was investigated in the case of pure SnO_2, by submitting a tin dioxide sample to the overall aqueous deposition method described above in the absence of any bismuth-containing precursor.

A reference catalyst was prepared from mechanical mixtures of SnO_2 with commercial Bi_2O_3 (Janssen, 99.9%), according to the same dispersion procedure in *n*-heptane.

All the catalysts prepared as described above were finally calcined at 803 K for 20 h under controlled air flow (1 ℓ/min).

Some other catalysts were prepared to elucidate the eventual role of the mixed bismuth pyrostannate phase, $Bi_2Sn_2O_7$. Three catalyst samples characterized by the same composition (10 wt% Bi_2O_3 on SnO_2) were prepared by mechanical mixture in *n*-heptane of tin dioxide and commercial Bi_2O_3 according to the procedure described above, but calcined at 803, 973 and 1033 K, respectively. For reference purposes, a 1 : 1 molar mixture of Bi_2O_3 and SnO_2 was prepared by dispersion in *n*-heptane and calcined at 1033 K in order to form pure bismuth pyrostannate.

All the catalysts prepared within the frame of the present work are summarized in table 1.

2.4. Measurements of the catalytic activity

Catalytic tests. The catalytic performances of these catalysts were evaluated in the total oxidation of isobutene into CO_2, using air, in the temperature range 603–673 K. The experimental set-up includes a U-shaped fixed-bed glass reactor (internal diameter 8 mm), temperature and mass flow regulation systems, and an on-line gas chromatograph for the analysis of the reagents and products. Before their use in the catalytic tests, the catalysts were pelletized into granules of 0.5–0.8 mm diameter. The amounts of catalyst used for each run were respectively 500 mg in the case of the pure oxides

Table 1
Description of catalyst preparation

Catalyst (support/ Bi_2O_3 precursor/wt%)	Deposition procedure	Medium	Calcination temperature (K)
SnO_2/–	–	–	803
SnO_2/–	dispersion	water	803
Bi_2O_3/–	–	–	803
SnO_2/Bi(OAc)$_3$/10	dispersion	n-heptane [a]	803
SnO_2/Bi(Hcit)/10	dispersion	n-heptane	803
SnO_2/Bi(Hcit)/10	dispersion	water	803
SnO_2/Bi(Hedta)/10	impregnation	water	803
SnO_2/Bi(nta)/10	impregnation	water	803
SnO_2/Bi(NO_3)$_3$/10	impregnation	water	803
SnO_2/commercial Bi_2O_3/10	dispersion	n-heptane	803
SnO_2/commercial Bi_2O_3/10	dispersion	n-heptane	973
SnO_2/commercial Bi_2O_3/10	dispersion	n-heptane	1033
SnO_2/commercial Bi_2O_3/155 [b]	dispersion	n-heptane	1033

[a] Under nitrogen.
[b] 155 wt% represents the equimolar mixture Bi/Sn = 1.

(SnO_2, Bi_2O_3, $Bi_2Sn_2O_7$), and 550 mg for the mechanical mixtures Bi_2O_3 (10 wt%)–SnO_2, in such a way that the amount of tin dioxide was always the same. Reagents were introduced as a mixture made of 96.6 vol% air and 3.4 vol% isobutene. Temperature control was ensured by chromel–alumel thermocouples dipped into the catalytic bed through a glass tube. The composition of the gaseous mixture at the reactor output was quantitatively analyzed with a gas chromatograph Intersmat IGC 12M, equipped with two 2.5 m long columns, one for the separation of isobutene, CO_2 and water (stationary phase Porapak), the other for the analysis of partial oxidation products (stationary phase Tenax). Helium was used as carrier gas and detection was made by catharometry. Formaldehyde was found as only side product in all the catalytic tests and accounts for the mass balance in the reactor. The production of methacrolein was never observed in our experimental conditions.

Expression of catalytic results. Catalytic results are expressed as isobutene conversion (X (%)), and yield in CO_2 (Y_{CO_2} (%)), representing the ratio of the number of CO_2 moles formed to the initial number of moles of isobutene in the reactor. This parameter will be tabulated as $Y_{CO_2}/4$ to allow for the formation of 4 moles of CO_2 per mole of isobutene converted.

2.5. Physical characterization techniques

Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D-5000 diffractometer using the Cu K_α radiation ($\lambda = 154.18$ pm).

X-ray photoelectron spectra were registered on a SSI-X-probe (SSX-100/206) spectrometer from Fisons, using the Al K_α radiation ($E = 1486.6$ eV) and a ceramic sample holder. Charge compensation was achieved by the use of a flood gun fixed at 10 eV. The binding energy scale was calibrated with respect to the C_{1s} photopeak of hydrocarbon contamination, taken at 284.8 eV.

BET specific surface areas were measured with a Micromeritics ASAP 2000 apparatus at 77 K, using either nitrogen or krypton as adsorbing gas, depending on the magnitude of the surface area.

3. Results and discussion

3.1. Physico-chemical characterization of the catalysts

3.1.1. XRD

For fresh and used catalysts previously calcined at 803 K, the amount of Bi_2O_3, as detected by XRD, is very low, especially for those which have been prepared by aqueous impregnation. All the Bi-loaded catalysts show in addition a low tendency to reduction of Bi(III) upon calcination of the used precursors, although this degradation step was carried out under controlled air flow rate conditions. There is no indication for the formation of bismuth pyrostannate at that temperature, neither before, nor after the catalytic test.

The presence of bismuth pyrostannate in the samples calcined at higher temperatures is clearly established; this phase is moderately abundant at 973 K but becomes a major component at 1033 K and its amount remains constant after use in the catalytic tests.

3.1.2. XPS

This technique was used to collect informations on the nature and dispersion of the various phases on the surface of the catalysts. More particularly, the atomic intensity ratios, listed in table 2, were determined for the various elements to get an idea of the surface stoichiometry of these catalysts. The analyses of tin, bismuth and

Table 2
XPS data and BET specific surface areas

Catalyst[a] (support/Bi_2O_3 precursor/calcination temperature (K))	Fresh catalyst				Used catalyst[b]			
	S_{BET} (m^2/g)	Bi/Sn[c]	C/Sn	C/Bi	S_{BET} (m^2/g)	Bi/Sn[c]	C/Sn	C/Bi
SnO_2/–/803	14.3	–	0.35	–	16.8	–	1.63	–
SnO_2/Bi_2O_3/803	12.5	0.035	0.41	11.9	14.5	0.073	1.57	21.6
SnO_2/Bi(Hcit)/803	11.8	0.14	0.47	3.3	–	0.23	0.94	4.0
SnO_2/Bi(Hedta)/803	14.4	0.34	0.54	1.6	12.7	0.34	0.73	2.2
SnO_2/Bi(nta)/803	14.9	0.35	0.56	1.6	13.9	0.34	0.57	1.7
SnO_2/$Bi(NO_3)_3 \cdot 5H_2O$/803	22.8	0.34	0.59	1.7	11.3	0.29	0.83	2.8
SnO_2/$Bi(OAc)_3$/803	13.4	0.37	0.82	2.2	12.9	0.38	0.77	2.0
SnO_2/Bi(Hcit)–heptane/803	9.1	0.32	0.62	1.9	9.6	0.24	1.10	4.6
SnO_2/Bi(Hcit)–H_2O/803	9.8	0.29	0.57	2.0	10.8	0.17	1.44	8.5
SnO_2/Bi_2O_3/803	–	0.022	0.13	13.7	10.5	0.083	3.0	35.9
SnO_2/Bi_2O_3/973	10.1	0.31	0.75	2.4	9.7	0.27	0.59	2.2
SnO_2/Bi_2O_3/1033	8.9	0.20	0.76	2.9	10.0	0.25	0.54	2.2

[a] All catalysts were calcined in air for 20 h. Bi-promoted catalysts contain 10 wt% Bi_2O_3.

[b] After catalytic test at 673 K.

[c] Bulk value corresponding to 10 wt% Bi_2O_3 on SnO_2 is 0.067.

oxygen were based on the following photopeaks: $Sn_{3d_{5/2}}$, $Bi_{4f_{7/2}}$ and O_{1s}; their binding energy values (E_b) are (486.7 ± 0.1), (159.4 ± 0.1), and (530.5 ± 0.1) eV, respectively. These values do not depend on the nature of the bismuth precursor used for the catalyst preparation and remain the same after catalytic use. The E_b values observed for the Bi and Sn photopeaks correspond to the standard values associated with Sn^{IV} and Bi^{III} species. All the bismuth-loaded catalysts show a low tendency to reduction of Bi(III) into Bi^0 ($E_b(Bi_{4f_{7/2}}) = 157.0 \pm 0.1$ eV) upon calcination (Bi^0/Bi^{III} around 0.05). The E_b values characteristic of the elements in the bismuth pyrostannate phase are (486.3 ± 0.1), (159.0 ± 0.1) and (529.8 ± 0.1) eV for $Sn_{3d_{5/2}}$, $Bi_{4f_{7/2}}$ and O_{1s}.

The main comments on the atomic intensity ratios listed in table 2 are the following.

(i) The Sn/O intensity ratios (not included in table 2) are always close to 0.5, which is the theoretical value for pure SnO_2. This is the case in fresh as well as in used catalysts. The same remark holds for the pure $Bi_2Sn_2O_7$ phase (Sn/O close to 0.29).

(ii) Closer attention has to be paid on the experimental Bi/Sn atomic ratios. All the catalysts prepared from Bi carboxylate precursors give rise to Bi/Sn ratios that are significantly larger than the bulk value calculated from the respective amounts of Bi-containing precursor and support. On the other hand, all the catalysts prepared from Bi_2O_3 itself display very low Bi/Sn ratios. These observations could most probably be interpreted as indicating the achievement of a better dispersion of the Bi-containing phase on the support when Bi_2O_3 is generated in situ from the carboxylate precursor. However, they could also be analysed in the light of the combined variations of the C/Sn and C/Bi ratios, which seem to influence directly the Bi/Sn ratios. As indicated in the bottom of table 2, the modification of the C/Sn and C/Bi ratios in the SnO_2–Bi_2O_3 mixtures calcined above 803 K actually results in a marked increase in the related Bi/Sn ratios.

(iii) In addition, the use of the Bi/Sn ratios to evidence the presence of bismuth pyrostannate is not straightforward. When comparing samples with similar amounts of surface carbon species, it appears that the catalysts calcined above 803 K, which were found to contain bismuth pyrostannate, show Bi/Sn ratios that are definitely identical with those of samples in which XRD failed to detect this phase. In the same way, when small amounts of bismuth stannate are formed on SnO_2, the differences in Sn_{3d} and Bi_{4f} binding energies do not allow one to detect the presence of this phase.

(iv) The comparison between the C/Sn ratios in the different Bi-loaded samples shows that carbon contamination in the fresh catalysts made from carboxylates is low and comparable to the level observed in pure SnO_2. This indicates that the experimental conditions selected for the thermal degradation of the Bi carboxylate precursors are able to ensure the absence of any significant surface contamination of the support with carbonaceous species, although the starting materials are rather carbon-rich.

(v) There is no significant coke formation during reaction. For comparable reaction times, the increase of C/Sn ratios in used catalysts is however more important in the unpromoted catalysts and in the Bi-loaded catalysts prepared from Bi_2O_3 itself than in those where bismuth oxide was generated from a carboxylate precursor. The same trends are observed for the C/Bi ratios. This ratio

Table 3
Isobutene conversion (%) at various reaction temperatures

Catalyst [a] (support/ Bi_2O_3 precursor/wt%)	$T = 603$ K	$T = 623$ K	$T = 648$ K
SnO_2/–	7.5	9.0	20.8
SnO_2/Bi_2O_3/10	7.8	8.8	19.9
SnO_2/Bi(Hcit)/10	12.4	27.6	68.0
SnO_2/Bi(Hedta)/10	11.6	18.2	29.2
SnO_2/Bi(nta)/10	9.2	17.7	36.4
$SnO_2/Bi(NO_3)_3$/10	6.3	13.3	32.9
$SnO_2/Bi(OAc)_3$/10	6.5	11.7	20.6
Bi_2O_3/–	0.0	0.0	0.0
$Bi_2Sn_2O_7$/–	1.6	3.0	6.0

[a] 500 mg for pure Bi_2O_3, SnO_2 and $Bi_2Sn_2O_7$; 550 mg for mixtures.

is much smaller in the Bi-loaded catalysts made from Bi carboxylate precursors than in the sample prepared from Bi_2O_3 itself.

3.2. Catalytic results

The catalytic performances of the various samples towards the total oxidation of isobutene are described in table 3 (isobutene conversion) and illustrated in figures 1 and 2 (yields in CO_2). Total isobutene conversion and yield in CO_2 behave similarly with respect to temperature and catalyst nature.

Figure 1 illustrates the influence of the presence of bismuth, and of its incorporation mode, on the CO_2 yield. It suggests the following comments:

(a) Because diffusion problems appear above 648 K for the most active catalysts, the interpretation of the results obtained at 673 K is not relevant for the present discussion.

(b) We checked the absence of any catalytic activity of pure Bi_2O_3 for the selected reaction in the temperature range 603–673 K. Similarly, pure α-bismuth pyrostannate displays only a very low activity, whereas pure SnO_2 becomes active around 648 K.

(c) Positive cooperative effects are clearly observed on both the CO_2 production and the total isobutene conversion in the case of Bi-promoted catalysts except in those where bismuth acetate and pure Bi_2O_3 were used as precursors. These effects are more significant when considering the bimetallic catalysts prepared from a dispersion of bismuth citrate. The three catalysts obtained from impregnation of SnO_2 with aqueous solutions of Bi-compounds precursors exhibit similar activities but are clearly less performant than the former ones. The bimetallic systems obtained by dispersing bismuth acetate or pure Bi_2O_3 in n-heptane behave as unpromoted SnO_2.

(d) The influence of the incorporation medium (n-heptane/water) was investigated for pure SnO_2 and the

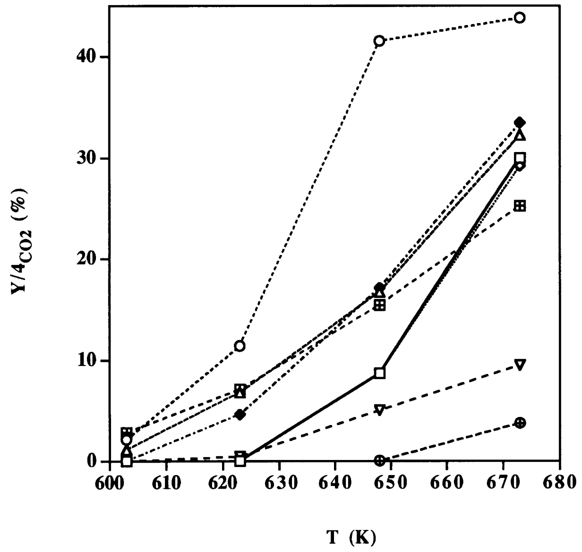

Figure 1. CO_2 production vs. reaction temperature for pure SnO_2 (□), $Bi_2Sn_2O_7$ (⊕), and various B_2O_3 (10 wt%)–SnO_2 catalysts prepared from Bi_2O_3 (◇), $Bi(OAc)_3$ (▽), Bi(Hcit) (○), Bi(nta) (△), Bi(Hedta) (⊞) and $Bi(NO_3)_3{\cdot}5H_2O$ (◆).

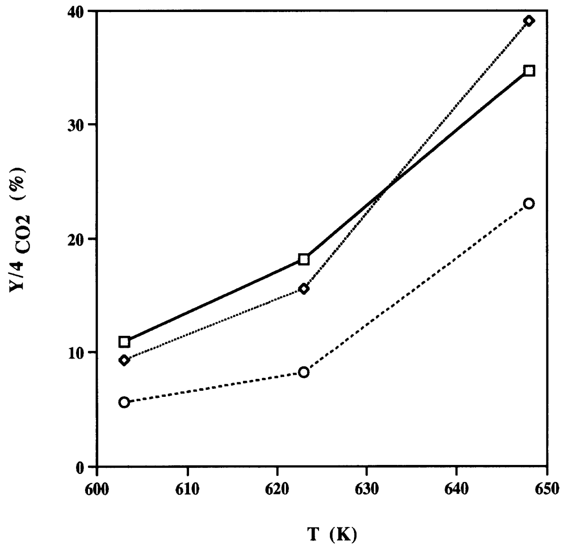

Figure 2. CO_2 production vs. reaction temperature for Bi_2O_3 (10 wt%)–SnO_2 mixtures calcined at 803 K (○), 973 K (◇) and 1033 K (□).

catalyst made by deposition of Bi citrate: we found no difference, neither on the BET specific surface area (table 2), nor in the catalytic performances.

Figure 2 describes the influence of the calcination temperature on the catalytic behaviour and illustrates the role played by the mixed $Bi_2Sn_2O_7$ phase. The samples calcined at 973 and 1033 K, which were shown by XRD to contain bismuth pyrostannate, also have the same specific surface area (ca. 10 $m^2 g^{-1}$) and display the same catalytic performances. They are rather active, and in any case, much more than the catalyst made from pure Bi_2O_3.

3.3. General comments and conclusions

Whereas pure SnO_2 is completely inactive for the total oxidation of isobutene below 648 K, most of the Bi-promoted SnO_2 catalysts show significant catalytic properties for this reaction. These cooperative effects which are observed on both the CO_2 production and the isobutene conversion are more important when the bimetallic catalysts are prepared by dispersion of bismuth citrate in *n*-heptane or in water. The samples containing simultaneously $Bi_2Sn_2O_7$ and SnO_2 display a rather high catalytic activity. On the other hand, pure bismuth pyrostannate displays a very poor activity for this reaction; furthermore, the presence of this phase is never revealed in the bimetallic catalysts in which the calcination temperature does not exceed 803 K, neither before nor after the catalytic test.

Concerning the catalysts in which only SnO_2 and Bi_2O_3 are detected, several hypotheses can be emitted to explain these experimental observations.

(a) A first keypoint is to evaluate the catalytic influence of Bi_2O_3 itself in these catalysts. As already shown in table 3, experiments performed with 500 mg Bi_2O_3 resulted in the absence of any isobutene conversion. However, the lack of activity of commercial Bi_2O_3 might be due to the low surface area of this sample and the higher activity of the SnO_2–Bi_2O_3 catalysts could be merely explained by the fact that the catalysts in which Bi_2O_3 is supported on SnO_2 are characterized by a higher Bi_2O_3 dispersion. In that case, the activity would be related to the exposed Bi_2O_3 surface area. To answer these questions several comments can be put forward.

(i) It should first be remembered that the absolute amount of Bi_2O_3 in the supported catalysts is only 50 mg instead of 500 mg for the reference test with pure Bi_2O_3.

(ii) There seems to be no simple relationship between the total surface area (table 2) and the catalytic behaviour. Whereas the BET specific surface area of commercially available Bi_2O_3 amounts typically to 0.2 $m^2 g^{-1}$, those of Bi_2O_3 samples obtained from the thermal degradation of the Bi(III) carboxylate compounds used as precursors in the present work were reported in a previous paper as being in the range 0.4–0.8 $m^2 g^{-1}$. More particularly, among the catalysts investigated in this work, the most performant one (SnO_2/Bi(Hcit)/803) displays a specific surface area which is about one half of that of a catalyst giving rise to a lower activity (SnO_2/$Bi(NO_3)_3 \cdot 5H_2O$/803). Moreover, two other supported catalysts characterized by comparable surface areas with respect to the former ones (SnO_2/Bi_2O_3/803 and SnO_2/$Bi(OAc)_3$/803) exhibit a catalytic activity similar to that of pure SnO_2.

For all these reasons, an interpretation based on this simple explanation has to be ruled out because it fails in accounting for the overall behaviour of these catalysts.

(b) If we admit the absence of the ternary phase $Bi_2Sn_2O_7$ in the catalysts calcined at 803 K, the catalytic behaviour of these samples could be assigned to a cooperation between SnO_2 and Bi_2O_3 for the total oxidation of isobutene.

(c) It should be remembered that detection of bismuth pyrostannate remains impossible, either by X-ray analysis, or by photoelectron spectroscopy when this phase is present in very low amounts in the catalyst. We are therefore not allowed to rule out the total absence of bismuth pyrostannate in the catalysts calcined at 803 K. In the latter case, a possible cooperation between tin dioxide and the in situ generated ternary phase could be invoked to account for the synergetic effects observed in this type of catalyst.

(d) A third hypothesis, related to the previous one, is the formation, during the catalytic test, of a pure bismuth pyrostannate phase so highly dispersed that it would become intrinsically active while remaining undetectable by X-ray analysis. Combinations of several hypotheses can also not be excluded.

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